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Foreign Technology Division
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by

V. I. Avdyunin, N. N. Bakhman, et al.

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The catalytic activity of Fe_2O_3 in the combustion of mixts. of NH_4ClO_4 with poly(Me acrylate), polystyrene, S, or carbon black was at a max. with 1-5% Fe_2O_3 and fell off markedly for mixts. contg. greater than 20-35% Fe_2O_3. In all cases, the effectiveness of Fe_2O_3 was less for mixts. of relatively higher uncatalyzed burning velocity than for those of lower velocity. Studies of the catalytic effect of Fe_2O_3 in mixts. contg. Me_4NClO_4 instead of NH_4ClO_4, in the reaction of which NH_3 and HCl are presumably absent, indicated that a single mechanism of catalysis cannot account for the effect of Fe_2O_3 on burning of perchlorate mixts. Mosk. Khim.-Tekhnol. Inst. Im. Mendeleeva, Moscow, USSR [AP1209459]

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Carbon Black						
Styrene						
Perchlorate						
Ammonia						
Catalyst Activity						

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П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

EFFECT OF IRON OXIDE ON COMBUSTION RATE OF MIXTURES WITH DIFFERENT PERCHLORATES

(Moscow Institute of Chemical Technology im. D. I. Mendeleyev)

V. I. Avdyunin, N. N. Bakhman, V. S. Nikiforov, A. Ye. Fogel'zang, and Yu. S. Kichin

In this work we study the effect of the nature of a fuel and an oxidizer on the catalytic activity of Fe_2O_3.

The first series of experiments was conducted with mixtures of ammonium perchlorate (PKhA) [ПХА] with fuels of very different compositions: polymethylmethacrylate (PMMA) [ПММА], polystyrene (PS) [ПС], carbon black, sulfur, and guanidine nitrate (NG) [НГ]. The second series of tests was conducted with different perchlorates: of ammonium, potassium (PKhK) [ПХК], formamidine (PKhF) [ПХФ], and tetramethyl ammonium(PKhTMA) [ПХТМА].

The grades of these substances: PKhA - technically pure, PKhK - pure, PMMA - technically pure, carbon black - technically pure, sulfur - sublimed sulfur, NG - analytically pure, Fe_2O_3 - analytically pure, PKhF and PKhTMA - synthesized and recrystallized from alcohol and water, respectively. All substances were desiccated; PKhA, PKhK, PKhTMA, and NG were ground in a vibration mill. By means of the PSKh-2 device $S_{уд}$ was determined and the average particle dimension d was calculated, which for PKhA ~ 9 μm,

PkhK ~ 10 μm, PKhTMA ~ 10 μm, PMMA ~ 3 μm, PS ~ 20 μm, carbon black ~ 3 μm, sulfur ~ 15 μm, NG ~ 10 μm, and Fe_2O_3 ~ 1.8 μm.

The components were mixed on tracing paper with a rubber cork and were pressed into brass cylinders with an inner diameter of 8 mm to a relative density of 0.92-1.0. The charges were combusted in a constant-pressure bomb in nitrogen at a pressure of 70 atm. A piezoelectric crystal pressure sensor was used to measure combustion time, and the average combustion rate was calculated. The effectiveness of the catalyst is described by the value $z = u/u_0$, where u and u_0 is the combustion rate of a composition with and without a catalyst.

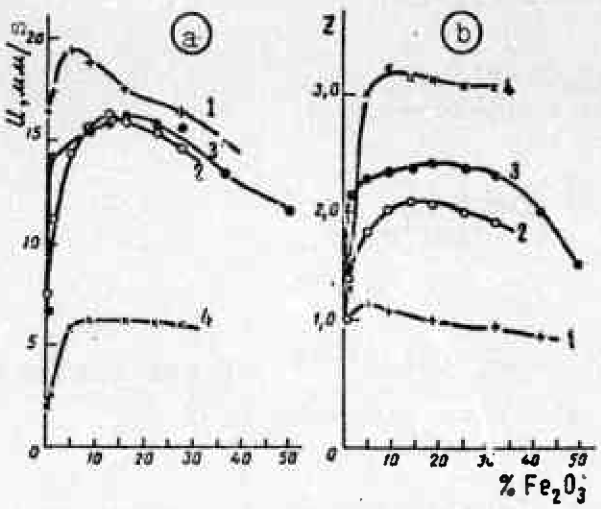

Fig. 1. Dependence of combustion rate (a) and effectiveness of catalyst (b) on per cent of iron oxide in mixture of PKhA + fuel ($\alpha = 0.6$; P = 70 atm). 1 - Sulfur; 2 - Carbon black; 3 - PMMA; 4 - NG.

In the first series of experiments we took curves u - % Fe_2O_3 and z - % Fe_2O_3 (see Fig. 1). The overall shape of the curves for all mixtures is the same, although on some curves there is a definite maximum (PKhA without fuel, all mixtures when $\alpha = 2$, and all mixtures with sulfur when $\alpha = 1$ and $\alpha = 0.6$)[1], while in other curves this shape represents a plateau (a mixture with carbon

[1] α - the stoichiometric coefficient: $\alpha = \frac{m_0/m_2}{(m_0/m_2)_{cmex}}$, where m_0, m_2 $(m_0)_{cmex}$, $(m_2)_{cmex}$ - are the parts by weight of the oxidant and the fuel in the given and the stoichiometric mixtures, respectively.

black, α = 1; a mixture with NG, α = 0.6). The increase in z with an increase in the % of Fe_2O_3 is steep, while the decline (to the right of z_{max}) is sloping. A catalyst effectiveness close to maximal ($z \approx 0.9\ z_{max}$) was reached at 1-5% Fe_2O_3 and was maintained right up to a concentration of Fe_2O_3 equal to 20-35%. However, values of z_{max} for mixtures with the studied fuels differ greatly. It seems that here the nature of the fuel does influence the effectiveness of the catalyst. Yet, if we plot the data for the different mixtures in coordinates z_{max}-u_0 (see Fig. 2), all of the points are grouped around one curve[1]. In this case the higher the combustion rate of the initial (without catalyst) mixture, the lower will be the effectiveness of the catalyst[2]. This means that the effect of the nature of the fuel is not specific: if we equalize values u_0 (for example, because of the oxidizer content), then the effectiveness of Fe_2O_3 in mixtures with the fuels which we have studied is the same.

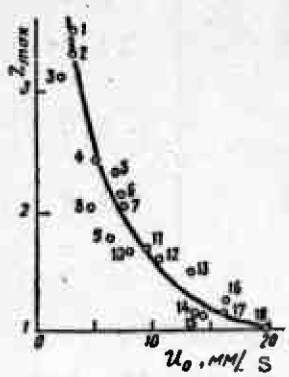

Fig. 2. Decline in effectiveness of Fe_2O_3 with an increase in the combustion rate of the original mixtures: 1 - PKhA + carbon black, α = 2.0; 2 - 77% (30% PKhA + 70% PKhTMA) + 23% PMMA; 3 - PKhA + NG, α = 0.6; 4 - PKhA + carbon black, α = 1.0; 5 - PKhA + PMMA, α = 0.6; 6 - PKhA + PMMA, α = 2.0; 7 - PKhA + carbon black, α = 0.6; 8 - PKhA + PS, $\alpha \approx$ 0.15; 9 - PKhA (without fuel); 10 - PKhA + PS, α = 2.1; 11 - 77% (50% PKhA + 50% PKhTMA) + 23% PMMA; 12 - (10% PKhK + 90% PKhA) + PMMA, α = 0.6; 13 - PKhA + PMMA, α = 1.0; 14 - (50% PKhK + 50% PKhA) + PMMA, α = 0.6; 15 - PHhA + PS, α = 0.3; 16 - PKhA + sulfur, α = 1.0; 17 - PKhA + sulfur, α = 0.6; 18 - PKhK + PMMA, α = 0.6.

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[1]In Fig. 2 the curve corresponds to the dependence $z_{max} \sim \frac{1}{u_0^{0.65}}$

[2]The value of z_{max} also declines with an increase in u_0 due to an increase in the initial temperature T_0 (for example, for a mixture of PKhA/PMMA when α = 1 at 20° C we have u_0 = 12.2 mm/s, z_{max} = 1.85; and at 150° C u_0 = 20 mm/s, z_{max} = 1.50). The position of z_{max} has a relatively weak dependence on T_0, yet with a decline in the combustion rate to the right of z_{max} it becomes more sloping with an increase in T_0 (Fig. 3).

Nevertheless, here we have a complicating factor: in any mixture based on PKhA the "total" fuel is a mixture of the "basic" fuel (for example, PS) and the ammonia[1], where the molecular fraction of the ammonia is very significant. Therefore, the absence of a specific effect in the nature of the "basic" fuel could be explained by the fact that Fe_2O_3 acts on the ammonia oxidizer.

We studied the effect of Fe_2O_3 on the mixture NH_4NO_3+ charcoal and the mixture PKhK + NG (pure and diluted NH_4Cl and NH_4HCO_3). In all of these cases Fe_2O_3 was not effective (see Table 1).

Table 1. Effect of Fe_2O_3 on the combustion of mixtures whose gasification products contain ammonia but do not contain perchloric acid

Mixture	u, mm/s		
	without Fe_2O_3	1% Fe_2O_3	5% Fe_2O_3
NH_4NO_3 + charcoal, $\alpha = 1$	2.8	2.4	2.4
PKhK + NG, $\alpha = 0.6$	19.4	18.8	17.[illegible]
85% (PKhK + NG, $\alpha = 0.6$) + 15% NH_4Cl	6.9	5.2	3.8
80% (PKhK + NG, $\alpha = 0.6$) + 20% NH_4HCO_3	10.0	9.8	8.5

Hence it follows that Fe_2O_3 either does not speed the oxidation of ammonia during combustion at all or speeds it, but only when the oxidizer is perchloric acid or its decay products. This is a problem which requires further study.

In the second series of experiments we tested the hypothesis that the effect of the catalysts on thermal decomposition and, possibly, on combustion of the perchlorates was related to the

[1]The drop in PKhA is according to the system $NH_4ClO_4 \rightleftarrows NH_3 + HClO_4$.

accelerated decomposition of perchloric acid [1-4]. From this standpoint Fe_2O_3 should be effective in compositions with PKhA and PKhF and should not be effective in compositions with PKhK and PKhTMA. Actually, Fe_2O_3 substantially accelerated the combustion of PKhF (without fuel; plexiglass shell with $d_{внутр}$ = 8 mm):

% Fe_2O_3	0	1	5	9.1	16.8	28.6
u, mm/s	13.5	26.4	27.7	26.0	24.0	19.9

The iron oxide had almost no effect on compositions with PKhK and PKhTMA, which, it seems, is in total agreement with the hypothesis concerning the role of the catalyst on the decomposition of $HClO_4$. Yet the combustion rate of these compositions is high, and judging from Fig. 2, this could be the reason for the low effectiveness of Fe_2O_3. Actually, when the value of u_0 for mixtures based on PKhTMA was reduced due to dilution, the effectiveness of Fe_2O_3 rose sharply (Table 2).

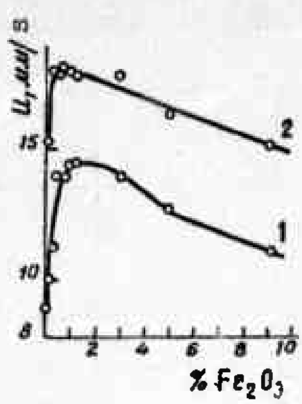

Fig. 3. Combustion rate of PKhA (without fuel) as a function of the per cent of iron oxide (tests with plexiglass shells at P = 100 atm). T_0, °C: 1 - 20; 2 - 100.

Since in the primary decomposition of PKhTMA neither perchloric acid nor ammonia are formed, we should turn our attention to other possible ways in which Fe_2O_3 could be effective (for example, associated with reactions of chlorine oxides).

As for mixtures based on PKhK, when their combustion rate was reduced by introducing KCl or Al_2O_3, the addition of Fe_2O_3

was, as before, not effective (see Table 3 for the composition of PKhK + PMMA).

Table 2. Effect of Fe_2O_3 on combustion of mixtures based on tetramethyl ammonium perchlorate containing different diluents.

Composition, %			u_{70atm}, mm/s		z
PKhTMA	PKhK	Diluent	without Fe_2O_3	1% Fe_2O_3	1% Fe_2O_3
85	15	–	27.1	28.2	1.04
90	10	–	20.1	22.2	1.10
77.3	13.6	9.1 NH_4Cl	14.0	23.7	1.69
70.7	12.5	16.8 NH_4Cl	8.5	18.8	2.21
65.4	11.5	23.1 Al_2O_3	6.3	16.2	2.58
52.7	2.8	44.5 KCl	5.2	11.7	2.25
55.5	–	44.5 KCl	4.4	9.7	2.20

Table 3. Effect of Fe_2O_3 on combustion of mixtures based on potassium perchlorate containing different diluents.

α	Diluent	$u_{70\ atm}$, mm/s			
		without Fe_2O_3	1% Fe_2O_3	3% Fe_2O_3	5% Fe_2O_3
2.0	–	12.8	–	13.7	–
2.0	16.7% KCl	8.8	9.0	–	9.1
0.4		14.2	14.8	14.7	14.9
0.4	13% KCl	11.9	12.25	–	11.3
0.4	23.1% KCl	8.6	9.0	–	8.7
0.4	16.7% Al_2O_3	8.1	8.3	–	–
0.4	50% Al_2O_3	2.6	2.8	2.7	2.8

We note in conclusion that the results obtained confirm the ideas of [5] concerning the concurrence of a homogeneous reaction in volume and a heterogeneous reaction in the catalyst. With an

increase in the rate of the homogeneous reaction[1] and, accordingly, with an increase in u_0 the contribution of the heterogeneous reaction (which also means quantity z) must decrease, which is observed experimentally.

One might think that the catalyst acts on one of the intermediate combustion stages Actually, z_{max} has already been reached with a relatively low per cent of Fe_2O_3. This is related to the fact that by accelerating the given stage the catalyst will accelerate the combustion rate only as long as one of the other stages does not become limiting.

CONCLUSION

The authors

1. ~~We~~ have studied the catalystic effect of Fe_2O_3 on the combustion of mixtures of ammonium perchlorate with five different fuels and of certain mixtures with perchlorates of formamidine, potassium, and tetramethyl ammonium.

2. For mixtures based on ammonium perchlorate the effectiveness of the catalyst, which is close to maximal, is reached with only 1-5% Fe_2O_3, while a substantial decline in its effectiveness is observed only at 20-35% Fe_2O_3.

3. In all cases the effectiveness of Fe_2O_3 decreases with an increase in the combustion rate of the original composition. The nature of the fuel was not observed to have a specific effect on the effectiveness of Fe_2O_3.

4. An acceleration in the decomposition of perchloric acid and an increase in the oxidation rate of ammonia are not the only

[1]As a result of the increased combustion temperature or the transition to a more active fuel (but not because of pressure, which can accelerate both the homogeneous and heterogeneous reactions).

possible ways in which Fe_2O_3 can be effective, since Fe_2O_3 effectively accelerates the combustion of dilute mixtures based on tetramethyl ammonium perchlorate, where perchloric acid and ammonia are absent.

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